

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Oxymethylene Polymers

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the preparation of oxymethylene polymers and to the oxymethylene polymers so prepared.

Oxymethylene polymers, sometimes known as polyoxymethylenes, are polymers having repeating units of the structure $\text{—O—CH}_2\text{—}$ and may be derived, for example, from the polymerisation of formaldehyde or its cyclic trimer, trioxane, as described in B.P. 748,836 and B.P. 877,820. The polyoxymethylenes prepared by normal homopolymerisation processes generally contain terminal oxymethylene hydroxide ($\text{—OCH}_2\text{OH}$) groups and have been found to be subject to degradation on heating at even quite moderate temperatures. In order to overcome this undesirable characteristic it has been proposed to react the hydroxyl end groups with compounds that will substitute for the relatively unstable hydroxyl group, an end group which is more stable, such as an acetate, ether or urethane group.

We have now found that useful high molecular weight oxymethylene polymers of good stability may be prepared by polymerising a cyclic oligomer of formaldehyde in the presence of certain polyformals.

According to the present invention we provide a copolymer comprising the product of polymerising a cyclic oligomer of formaldehyde, preferably trioxane, with a polyformal as hereinafter defined.

[Price 4s. 6d.]

Of the cyclic oligomers of formaldehyde we prefer trioxane because of its ready availability. Tetraoxymethylene is an example of another such cyclic oligomer.

By a polyformal, we mean a polymer having in the polymeric chain the recurring unit $\text{O—CH}_2\text{—O—R—}$ where R is a divalent organic radical derived from a diol by removal of the two hydroxyl groups and R may vary in the units along the chain and may be a $\text{—CH}_2\text{—}$ group provided that there are sufficient —R— groups having at least two adjacent carbon atoms in the polymer chain for the polyformal to contain at least 20% of such —R— units based on the total number of —R— and $\text{—CH}_2\text{—}$ units in the polyformal.

Our preferred polyformals are those in which the radical —R— remains the same in the chain and preferably in which the chain has the structure $\text{XO—(CH}_2\text{—O—R—O)}_n\text{Y}$ where n is a whole number and X and Y are hydrogen or monovalent organic radicals.

The polyformals may be derived from the diols, for example, by reacting them with formaldehyde or with a formal such as dibutyl formal with the elimination of an alcohol.

Suitable diols which may be used include (i) glycols having the structure $\text{HO(CH}_2)_n\text{OH}$ or their substituted derivatives in which n is at least 2 and the substituents may be alkyl, alkenyl, aryl or aralkyl groups or halogen atoms provided the latter are not geminal to any of the hydroxyl groups, (ii) dihydric alcohols having unsaturated linkages in the chain between the hydroxyl groups, (iii) dihydric alcohols having the structure $\text{HO(CH}_2)_a\text{—Z—(CH}_2)_b\text{OH}$ where a and b are whole numbers one of which is 2 or more and Z is a

divalent atom or group having the structure $-\text{S}-$, $-\text{O}-$, $-\text{SO}-$, $-\text{SO}_2-$ or $-\text{CO}-$, and the hydrogen atoms of the methylene groups may be substituted, if desired and (iv) dihydric alcohols containing an aromatic nucleus between two hydroxy-methylene groups and (v) cyclo-alkylene glycols.

Examples of diols that may be used are ethylene glycol; diethylene glycol; triethylene glycol; propylene glycol; hexamethylene glycol; decamethylene glycol; 1,3-cyclobutanediol; 1,1,3,3-tetramethyl-2,4-cyclobutanediol; 1,4-cyclohexane diol; bis(1,4-hydroxymethyl)-cyclohexane; neopentyl glycol, the isomeric xylylene glycols, unsaturated diols such as but-2-ene-1,4-diol and pent-2-ene-1,4-diol, di-(2-hydroxyethyl) thioether; di-(2-hydroxyethyl) sulphone and di-(2-hydroxyethyl) ketone. Homologues of these dihydroxy compounds and their substituted derivatives may also be used.

We prefer to use polyformals derived from diols containing a phenylene group in the chain between the hydroxymethylene groups as copolymers formed from these polyformals have a useful thermal stability.

The polyformals may also be obtained from the polymerisation of cyclic formals of which 1,3-dioxolane, 1,3-dioxane and 1,3,6-trioxacyclo octane are to be preferred because of their ready availability. Unsaturated cyclic formals such as that from but-2-ene-1,4-diol and formaldehyde which polymerise to give an unsaturated polyformal may also be used and the copolymers derived from these polyformals may be chemically modified if desired.

The polyformals may be end-group stabilised by thermal degradation or degradation by mild acids or bases as hereinafter described for the polymers but normally this is unnecessary. Alternatively they may be stabilised by reacting the end group of the polyformal with a suitable reagent giving a stable end group as is described hereinafter for the polymers.

The preferred polyformals for use in the process of our invention are those that are soluble in molten trioxane or in the mixture of trioxane and solvent if a solution polymerisation process is to be used.

We prefer the polyformals to have a molecular weight of at least 1,000 and preferably at least 3,000. The use of polyformals having molecular weights below 1,000 to form our copolymers tends to give products of low molecular weight, generally unsuitable as moulding materials, because of their chain transfer characteristics. As the molecular weight of the polyformal increases, so in general does the molecular weight of the final copolymer increase. However, such increase decreases the solubility of the polyformal in trioxane and we prefer to use those

polyformals having a molecular weight of from about 3,000 to about 8,000.

In order to obtain products of good physical properties, it is preferred that the copolymers contain more than 80% molar of oxymethylene ($\text{O}-\text{CH}_2-$) units. Copolymers containing at least 90% molar of such units are tough, rigid and very suitable for moulding. We prefer that the copolymer contains at least 0.1% molar and preferably at least 0.5% molar of units other than oxymethylene units since the presence of smaller amounts of these units has not, in general, sufficient effect upon the thermal stability of the copolymer. Copolymers containing from 1.5 to 5 molar % of such units have useful stability and rigidity and are good moulding materials.

Particularly useful polymers are obtained when their molecular weight is at least 15,000 and preferably 20,000 or more. A molecular weight of 20,000 is approximately equivalent to an Inherent Viscosity of 1.0 as measured as a 0.5% solution in p-chlorophenol containing 2% of α -pinene at 60°C.

Further according to the present invention we provide a process for the preparation of high molecular weight oxymethylene polymers which comprises polymerising together a cyclic oligomer of formaldehyde and a polyformal as hereinbefore defined, the polymerisation being carried out in the presence of an electrophilic catalyst and in the presence of no more than a very small amount of water.

The process of the invention is a useful method for inserting into the polymer chain units which could not otherwise be placed there such as long chain alkylene units, and units containing phenylene radicals in the chain between the oxygen atoms (e.g. xylylene units).

The polymerisation may be effected in bulk or in solution.

Where a bulk process is used, the polymerisation is normally carried out at a temperature at which the polymerisable material is in a molten or substantially molten form. However, for the preparation of high molecular weight polymers, e.g. polymers of molecular weight greater than 15,000 the polymerisation temperature should not be so high as to allow substantial depolymerisation to occur. It is preferred, on the other hand, that a temperature is used at which the polyformal is soluble in trioxane.

It is preferred to effect the polymerisation at temperatures of from about 0° to about 100°C. and preferably 50–90°C. but higher temperatures may be used if desired. Where it is desired to use temperatures of above about 115°C. (the boiling point of trioxane) the polymerisation should be carried out under super-atmospheric pressure.

Where the polymerisation is effected in

solution, the polyformal is preferably one which is soluble in the mixture of trioxane and solvent. Suitable solvents include hydrocarbons such as hexane, heptane, cyclohexane, benzene, toluene and xylene, and chlorinated hydrocarbons such as methylene chloride, chloroform or carbon tetrachloride. It is preferred to effect the polymerisation at a temperature high enough to prevent the polymerisable compound from crystallising out of solution but at a temperature not above the boiling point of the solution at the working pressure. The polymerisation may be effected under super-atmospheric pressure if desired and this is useful since it permits higher temperatures to be used.

The polymerisation may take place satisfactorily in the presence of very small amounts of water such as would be found as impurities in the oligomer or the polyformal but if good yields of high molecular weight material are to be obtained it is preferred to remove substantially all traces of water from the polymerisation medium.

Any electrophilic catalyst may be used in the polymerisation and examples of these are Lewis acids, Friedel-Craft catalysts, elementary iodine, perchloric acid and acetyl perchlorate. Of these, Lewis acids which are halides are preferred and boron trifluoride in particular has been found to give very good results. The boron trifluoride may be used in unmodified form or as one of its complexes; examples of such complexes include those with water, with organic compounds having an oxygen or sulphur atom which may act as the donor atom (e.g. alcohols, ethers, acids and their sulphur analogues), with organic compounds having a trivalent nitrogen or phosphorous atom (e.g. amines and phosphines) and fluoborate complexes such as those with diazonium compounds. The amount of catalyst used is generally from 0.0001 to 0.1 parts by weight of active constituent per 100 parts by weight of monomeric material when it is desired to form high molecular weight products suitable for moulding and similar processes.

The molecular weight of the products of the invention may be controlled by adding chain transfer agents to the polymerisation medium, suitable chain transfer agents being chlorinated hydrocarbons, alkyl acetates and acetals. It is preferred to effect the polymerisation in the substantial absence of oxygen.

We prefer that the polymerisation is effected in bulk or in the presence of only very small amounts of solvent since then the necessity of expensive solvent extraction and recovery processes may be avoided.

In a process according to our invention, the polyformal and trioxane are first carefully dried and are then added to a pre-dried reactor such as a steel bomb. The con-

tainer may be swept with nitrogen gas and the catalyst is then added alone or as a solution in an inert organic solvent. The container is sealed and heated to about 65°C. and the polymerisation is allowed to take place. After the required time, the polymerisation is brought to a conclusion and the reactor will contain the polymeric products, unreacted trioxane, unreacted polyformal and catalyst residues.

In the production of high polymers as described above the polymerisation temperature is normally less than the softening point of the polymers. As the polymers formed are usually insoluble in the mixture of monomers, the product of a bulk polymerisation process is usually a crumbly mass. To ensure good mixing of the polymerisation and so full growth of the polymer chains, and to form an easily worked powder at the end of the polymerisation, it is desirable to apply shear to the polymerisation mixture during the bulk process.

Conditions of shear may be imposed by any suitable means, such as intense stirring or agitation and the polymerisation may, for example, be carried out in a vessel rotatable on a horizontal axis and having within it freely rolling spheres, rods or the like as described in the specification of British Patent No. 749,086. Very good results may be obtained if the polymerisation ingredients are fed into a continuous mixer having a screw with an interrupted thread placed in a cylindrical body the inside surface of which has rows of protruding teeth. The screw is made both to rotate and reciprocate so that the teeth on the wall of the cylindrical body pass through the breaks in the screw thread. In this case the polymerisation mass moves forward along a path which has a generally helicoidal shape with an alternate forward and backward movement as it moves towards the outlet. The use of this mixer also has the advantage in that a continuous process may be used. A suitable machine is described in the specification of British Patent No. 626,067.

Therefore, in another process according to the invention the polyformal and trioxane are first carefully dried and then added together with the catalyst to the pre-dried mixer which is heated to the desired temperature. The polymerisation takes place in the mixer which may be pressurised if desired and the polymer is removed from the other end of the mixer in the form of a slurry or powder.

The material so obtained will contain the polymeric product, catalyst residues and possibly unreacted trioxane and unreacted polyformal; the polymeric product comprises the copolymer of trioxane and the polyformal and possibly incidental polyoxymethylenes derived from the homopolymerisation of the trioxane. The catalyst residues are prefer-

ably removed as soon after the polymerisation as possible since their presence may also catalyse the decomposition of the polymeric product; they may be removed simply by washing the mix with an aqueous, preferably an aqueous alkaline wash. For example, the mix may be washed with a dilute ammoniacal or caustic soda solution. As is well known, solvents may also be used for removing these catalysts. During their removal the polymer may also be stabilised as is set out below.

The unreacted trioxane and any of the polyformal may be separated from the copolymer by any suitable means such as filtration or solvent extraction. Since trioxane is soluble in most common solvents, it may be separated by a solvent extraction process, e.g. at the same time as the catalyst is removed. The polyformal may also be extracted by a solvent extraction process.

The presence of the incidental polyoxymethylene may adversely affect the stability of the material and this may be remedied either by preferential destruction or by end-group stabilisation of this polyoxymethylene.

The copolymers prepared by the process of the invention contain both oxymethylene groups derived from the trioxane and divalent organic radicals containing two or more adjacent carbon atoms in the polymer chain derived from the polyformal and the copolymer chains may therefore be ended by terminal groups of the structure $\text{—O—CH}_2\text{OH}$ or they may be ended by other groups derived from the polyformal. Where a copolymer chain is terminated by a $\text{—O—CH}_2\text{OH}$ group, which is readily detachable on heating or under alkaline conditions, the end of the chain may be represented as having the structure $\text{—P—O—(CH}_2\text{O)}_n\text{H}$ where n is a whole number and P is the divalent organic radical containing two or more adjacent carbon atoms in the polymer chain derived from the polyformal and nearest to the end of the polymer chain. On subjecting the copolymer chain to a thermal or alkaline degradation reaction, the $\text{—O—CH}_2\text{OH}$ group will be detached and the oxymethylene group immediately behind it (if any) will receive a hydrogen atom and become an $\text{—O—CH}_2\text{OH}$ group and the chain will now have the structure $\text{—P—O—(CH}_2\text{O)}_{n-1}\text{H}$. This next $\text{—O—CH}_2\text{OH}$ group is now attacked and the degradation of the chain will continue until the —P—O— group is reached. Since the P—OH group is relatively much more resistant to detachment, the degradation reaction will normally halt there. The copolymer may therefore be stabilised either by subjecting it to such a degradation reaction or by end-group stabilising it. It will be appreciated that under such degradation conditions, any homopolyoxymethylene that may be present will eventually be de-

graded completely if conditions are sufficiently forcing.

Where it is preferred to destroy the incidental polyoxymethylene and to remove the unstable oxymethylene end-groups from the copolymer, this may be done simply by heating the mixture in an inert atmosphere, e.g. under nitrogen at a temperature of about 160°C . or above after the catalyst residues have been removed; it is preferred not to use too high a temperature since otherwise the copolymer may also be degraded to an undesirable extent. The preferential destruction may also be aided by the addition of a weak acid such as formic acid or acetic acid or an alkali such as caustic soda but the latter is not to be preferred as it may tend to cause undesirable degradation of the copolymer and may convert the formaldehyde so generated into sugar-like polymers.

Stabilisation by removal of these unstable entities may be carried out in an alkaline process for removing the polymerisation catalyst and in this preferred process, the polymer is treated with a basic, preferably ammoniacal, solution at moderately elevated temperatures. However, it is believed that the action of the basic solution may be merely topochemical (see, for instance, pages 231 and 232 of *Die Hochmolekularen Organischen Verbindungen* by Staudinger 1932) and for an efficient reaction the polymer is preferably treated either in a finely divided state or in solution and the formation of a solution may be encouraged by carrying out the process under elevated pressure and temperature. The advantage of such a process is that in one step the catalyst, unreacted trioxane and incidental homopolyoxymethylenes may all be removed from the polymer. When the solution is cooled, the desired stable oxymethylene copolymer comes out of solution and may be separated.

Instead of a strong, ammoniacal solution, a solution of an amine, or an amide or an alkali hydroxide such as sodium or potassium hydroxide or a salt of a strong base and weak acid such as sodium carbonate or sodium acetate may be used alone or in combination under similar conditions. The solvent may be water or preferably a mixture of water with a water-miscible alcohol, with a water-miscible ketone such as acetone or with an ether. The presence of the organic material helps to bring the polymeric material into solution.

When on the other hand it is preferred to end-group stabilise the incidental homopolyoxymethylene and the oxymethylene end-groups of the copolymer, the mixture may be reacted with any suitable compound which will substitute for the terminal hydroxyl group of the polyoxymethylene or copolymer other groups (such as acetate, ether or urethane groups) which are relatively more stable.

The end-group stabilisation may be effected for example, by reacting the copolymer mixture with a carboxylic acid, a carboxylic acid ester, a carboxylic acid anhydride, an alcohol, an acetal, an isocyanate, an ortho ester, a ketal, an ortho carbonate, a ketone, a ketene/ketone transformation product, an ether or their substituted derivatives, an epoxide such as ethylene oxide or propylene oxide, an olefine such as butadiene or styrene, an alkyl halide such as tertiary butyl chloride or a vinyl monomer such as acrylonitrile or acrolein. Reaction with a carboxylic acid anhydride such as acetic anhydride is preferred.

The copolymer may be further stabilised against degradation by the addition of any suitable stabiliser for the polyoxymethylene. Suitable stabilisers include, for example, hydrazines, amines, amidines, amides, polyamides, phenols, substituted phenols, poly-nuclear phenols (particularly alkylene bis-phenols), ureas, thioureas, quinones such as those described in our copending applications nos. 41039/61 (Serial No. 1031701) and 3474/62 (Serial No. 1031701) and certain aromatic nitro compounds, such as those described in our copending application number 3473/62 (Serial No. 1031708), alone or in combination. Stabilisers against attack by ultra violet light, such as hydroxy-substituted benzophenones, may also be incorporated into the polymer. Fillers, pigments, mould release agents, lubricants, plasticisers and the like may also be added and the polymer may be blended with other compatible polymeric materials.

The copolymers of the present invention differ from the products of homopolymerising trioxane. The melting points of the copolymers are lower than that of the crystalline homopolymer and the drop in melting point increases with increase in the amount of polyformal residue in the copolymer.

Also, the melting points of the copolymers are less sharp than that of the homopolymer and the decrease in definition becomes more marked as the amount of polyformal residue in the copolymer increases. For example, the homopolymers of trioxane have a crystalline melting point of 170°C. and the product of polymerising trioxane with 5% by weight of a polyformal derived from p-xylylene glycol has a melting range of 155–160°C.

The large drop in melting point of the copolymers and the wide melting range both indicate that the copolymers are of the random variety and are not block copolymers. Block copolymers having such small amounts of the polyformal would be expected to have melting points much closer to that of the homopolymer derived from trioxane and to have a narrower melting range.

Because of the width of melting range of our copolymers, the conditions required for moulding or otherwise fabricating them in massive form are not as critical as those required for the homopolymer and they lend themselves, therefore, to easier fabrication and are of particular interest for film-forming compositions. These copolymers, therefore, are commercially more attractive as moulding materials than the homopolymers.

The rate of thermal degradation of the copolymers, particularly of those which have been stabilised by the methods described, is substantially less than that of the homopolymer. For example, the rate of loss in weight at 222°C. of a homopolyoxymethylene derived from trioxane is about 3% per minute while the equivalent rates for our copolymers which have been subjected to an ammoniacal wash treatment are generally less than 0.5% per minute and may be as low as 0.03% per minute. This surprising stability at temperatures well in excess of their melting points makes these copolymers suitable in the manufacture of articles which may be subjected during their life to elevated temperature (for example as insulants in electrical switch gear).

Our copolymers containing at least 90 molar % of oxymethylene groups are tough and dimensionally stable at or above room temperature and their very low rate of thermal degradation makes them particularly useful as moulding materials (e.g. for use in injection moulding, compression moulding and extrusion processes) and for the melt-spinning and casting of fibres and films. We prefer our mouldable polymers to have a softening point of at least 150°C. They may also be solvent cast to give film or solvent spun to give fibres from suitable solvents, examples of which are o- and p-chlorophenol, benzyl alcohol and α -naphthol. These polymers may be used, for example, in the light engineering industry for the manufacture of small gears, roller bearings, bushes, clips and cams; in the motor industry for the manufacture of dust covers or caps for grease nipples and bearings such as track-rod joints, lamp covers, instrument housings, low stressed gears such as oil pump gears, speedometer gears and windscreen wiper gears, self-lock nuts and other small mouldings. Our copolymers containing lesser amounts of oxymethylene groups have reduced strength, rigidity and softening point, but are suitable as plasticisers, lubricants, etc. Those polymers derived from polyformals of unsaturated diols are suitable in applications where chemical modification of the products is desirable.

The invention is illustrated by the following Examples in which all parts are expressed as parts by weight.

EXAMPLE I

20 parts of trioxane (containing less than

0.001% moisture) and 1 part of a poly-(ethylene glycol formal) having a molecular weight of approximately 6,000 were dissolved in 13.5 parts of dry n-heptane, the solution was heated and stirred under an atmosphere of dry nitrogen at a bath temperature of 80–100°C. and 0.1 part of boron trifluoride etherate was added. After a brief interval polymerisation commenced, and heating and stirring under nitrogen were continued for a further 5 hours after which the mass was cooled. The cold mixture was filtered and the solid was ground finely with acetone, filtered, then washed twice more by resuspension in acetone, to give 16.5 parts of a white solid. This was suspended in a mixture of 9 parts of concentrated aqueous ammonia, 40 parts of water, and 8 parts of methanol and the suspension heated just below its boiling point for 2 hours, then filtered, washed several times with water and dried under vacuum to give 13.5 parts of polymer. 0.9248 part of this polymer were heated in the vapours of boiling methyl salicylate at 222°C. for 20 minutes under nitrogen. Upon cooling the solid and reweighing it, 0.7555 part remained. After a further 20 minutes at 222°C. the weight of this same sample had only decreased to 0.7462 part.

EXAMPLE II

Poly(ethylene glycol formal) was prepared as follows: a mixture of 90 parts of pure dioxolane and 0.18 parts of concentrated sulphuric acid was heated for 5 hours under a reflux condenser at a bath temperature of 110°C. whereby it was converted to a viscous syrup. 1 part of triethylamine was now added, followed by 2 parts of phenylisocyanate and this mixture stirred for 3 hours at a bath temperature of 100–110°C. The stirrer was removed and the mixture now heated at a bath temperature of 150°C. under a vacuum of 1 mm. of mercury. On cooling the product set to a hard waxy solid, and its infra-red spectrum showed a complete absence of hydroxyl groups.

4 parts of this poly(ethylene glycol formal) and 25 parts of substantially anhydrous trioxane were melted together in a glass vessel under an atmosphere of nitrogen to give a homogeneous solution which was then resolidified by cooling in a mixture of acetone and solid carbon dioxide. 0.03 part of boron trifluoride etherate was added to the cooled solution in the glass vessel, which was now sealed, brought up to and held at a temperature of 100°C. After an induction period of about 2 hours, polymerisation proceeded quite rapidly and the vessel was heated for a further 3 hours. The vessel was now opened and the contents were ground with ethanol containing 1% tri-n-butylamine, then filtered. The resultant solid was mixed in a homogenizer with 100 parts of cold 15%

aqueous, ammonia solution, filtered, remixed in the homogenizer with 100 parts of an aqueous solution containing 20% sodium sulphite and 1% sodium carbonate and re-filtered. The polymer was finally washed with water several times in the homogenizer and dried under vacuum. 17 parts colourless polymer were obtained. After heating 0.9410 part for 20 minutes at 222°C. under nitrogen as described in Example I, 0.8690 part remained, which decreased to 0.8214 part after a further 20 minutes at this temperature.

EXAMPLE III

A polyformal was prepared from para-xylylene glycol (1,4-bis-hydroxy-methyl benzene) as follows: A mixture of 27.6 parts of para-xylylene glycol, 30 parts of 30% aqueous formaldehyde solution and 1.2 parts of concentrated hydrochloric acid was distilled to remove water at a pressure of 12 mm. mercury and a bath temperature of 50°C. for 2 hours. The pressure was then lowered to 0.5 mm. and the temperature raised to 80°C. for a further 2 hours. 0.05 part D-camphor-10-sulphonic acid was then added and the mixture heated at 200–220°C. and 0.5 mm. until no further distillation could be detected. A residue of 31.5 parts of poly-(p-xylylene glycol formal) was thus obtained, being a waxy solid of m.pt. 79.5°C. and having a molecular weight of 3,000.

1.5 parts of this poly-(p-xylylene glycol formal) and 20 parts of pure trioxane were melted together in a glass tube to give a homogeneous solution which was cooled to –40°C. under nitrogen. 0.02 part of boron trifluoride diethyl etherate was added to the cooled solution, the tube was then sealed, and heated for 4 hours at 100°C. A polymer was produced which was recovered by breaking open the tube. The polymer was ground, washed with hot water in a homogenizer, filtered, washed with acetone by suspension, and then on a filter and finally reslurried with hot water in a homogenizer. The polymer was then suspended for 2 hours in a gently refluxing mixture of 18 parts of concentrated ammonia, 40 parts of water, and 16 parts of ethanol, and afterwards filtered and dried. A final yield of 14.6 parts of polymer was obtained.

0.9480 part of the polymer was heated at 222°C. under nitrogen for 20 minutes as described in Example I after which 0.8248 part remained, which reduced after a further 20 minutes at 222°C. to 0.7880 part.

EXAMPLE IV

0.1 part of the polyformal prepared as in Example III was dissolved in a mixture of 20 parts of substantially anhydrous trioxane and 3.5 parts of n-heptane and the mixture was stirred and heated at 70°C. under nitro-

gen. To the resultant solution was added 0.01 part of ferric chloride dissolved in 0.7 part ether whereupon polymerisation commenced and was completed by heating for a further 2 hours at 70°C.

The solid product was ground with acetone, filtered and washed successively with sodium carbonate solution followed by water. The finely divided polymer was then heated for 4 hours at 150°C. in a sealed vessel with 3.5 times its weight of a mixture of 10 parts of water, 13 parts of concentrated ammonia solution and 20 parts of ethanol. 9.4 parts of the polymer were recovered by filtration, having an inherent viscosity of 1.07 and containing 0.72% by weight of $-\text{CH}_2\text{C}_6\text{H}_4-\text{CH}_2\text{O}-$ units in the polymer. (C, 40.31; H, 6.80).

A weighed portion of the polymer was heated for two consecutive 20 minute periods at 222°C. as described in Example I. Assuming that its rate of weight loss showed approximately First Order kinetics, the weights remaining corresponded to breakdown rates of 0.23 and 0.19 per cent per minute respectively.

EXAMPLE V

To a mixture of 0.2 part of poly(p-xylylene glycol formal), prepared as in Example III, 20 parts of purified trioxane and 3.5 parts of n-heptane stirred at 82°C. under nitrogen was added a solution of 0.001 part of anhydrous ferric chloride dissolved in 0.7 part of ether. Polymerisation commenced after 30 minutes and thereafter the mixture was maintained at 80°C. for 2½ hours. The polymer obtained was washed first by grinding with hot dilute aqueous potassium hydroxide solution, then with hot water and was finally subjected to the same treatment with aqueous alcoholic ammonia as in Example IV. The resultant polymer had an inherent viscosity of 1.0 (measured as in Example IV). Assuming First Order kinetics for its rate of breakdown at 222°C. the rates over consecutive 20 minute periods were 0.065 and 0.025 per cent per minute respectively.

EXAMPLE VI

To a mixture of 20 parts of recrystallised trioxane and 3.5 parts of n-heptane was added 1 part of poly(p-xylylene glycol formal) of molecular weight 3,000 and prepared by the process of Example III. The mixture was brought to 70°C. under nitrogen and stirred and to it was added 0.0015 part of ferric chloride in 0.7 part of diethyl ether. Polymerisation was rapid and was completed by heating at 70°C. for 1 hour. The product was ground, washed with acetone followed by hot aqueous ammonia and was then refluxed with a mixture of 13 parts of concentrated aqueous ammonia, 40 parts of water and 8 parts of ethanol to yield 12.5 parts of a

copolymer containing 5% by weight of $-\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}-$ units (C, 42.03; H, 7.00).

The rates of weight loss of the polymer over consecutive 20 minute periods were 0.55% per minute for the first period and 0.18% per minute thereafter, reducing to give an overall average rate of 0.17% per minute over a 140 minute period.

The melting range of the polymer was found to be 155–160°C.

The rate of weight loss of a homopolymer of trioxane formed under similar conditions is about 3% per minute and its melting point is 170°C.

EXAMPLE VII

0.2 part of poly(p-xylylene glycol formal) of molecular weight 3,780, prepared by the process described in Example IV, and 0.0025 part of anhydrous ferric chloride were dissolved in 6 parts nitrobenzene and the resultant solution was injected into a mixture of 20 parts of purified trioxane and 3.5 parts n-heptane stirred at 70°C. under nitrogen. Polymerisation commenced immediately and was completed by heating for 2 hours at 70°C. The resultant polymeric mass was ground, washed and ammonia treated as in Example IV. The colourless polymer had an inherent viscosity of 1.0. After heating 0.7092 part for 20 minutes at 222°C. under nitrogen as described in Example I, 0.6707 part remained which decreased to 0.6438 part after a further 20 minutes at this temperature.

EXAMPLE VIII

A mixture of 28.8 parts of 2,2,4,4-tetramethylcyclobutane-1,3-diol, 7.6 parts paraformaldehyde and 0.1 part D-camphor-10-sulphonic acid was refluxed in 35 parts benzene, water being removed from the condensed vapours in a Dean and Stark separator. After 2 hours 0.6 part paraformaldehyde was added and heating continued for a further hour. Benzene was then stripped off the reaction mixture at 80°C. and 12 mm. of mercury. On allowing the residue to cool a colourless, solid polyformal was obtained.

A mixture of 1.5 parts of this polyformal, 15.8 parts of pure trioxane, and 10.5 parts n-heptane was stirred and heated in a glass vessel at 80°C. under an atmosphere of nitrogen until a homogeneous solution was obtained, whereupon 0.02 part of boron trifluoride diethyl etherate was added. Brisk polymerisation occurred after a brief induction period, and the mixture was stirred and heated at about 80°C. for a further 45 minutes. Afterwards the mixture was cooled and then diluted with acetone containing a little triethylamine. The suspended polymer was finely ground, filtered and rewashed

with fresh acetone. It was then slurried in a homogenizer with hot aqueous 5% ammonia, filtered and simmered gently for four hours, with a mixture of 60 parts of water, 14 parts of concentrated aqueous ammonia and 12 parts of ethanol. 8.5 parts of a colourless polymer were obtained after filtration and drying.

1.0000 gm of the polymer was heated for 20 minutes at 222°C. as described in Example I whereafter 0.8788 g. remained, which reduced after a further 20 minutes at 222°C. to 0.8637 g.

EXAMPLE IX

The polyformal of but-2-ene-1,4-diol was prepared by heating together a mixture of 88 parts of the diol, 32 parts of paraform, 0.5 part of Amberlite 1R-120(H) resin and 440 parts of benzene in an apparatus fitted with a Dean and Stark separator until approximately 18 parts of water had been removed. The Amberlite resin was filtered off and the benzene and cyclic formal (formed as a by-product) removed by distillation. The viscous liquid was then heated for 4 hours at 220°C. under 0.5 mm. Hg. pressure.

Into a mixture of 20.5 parts of dry trioxane and 2.05 parts of the polyformal at 70°C. was added 0.023 part of boron trifluoride-diethyl etherate. Polymerisation was rapid and after 15 minutes the pale brown solid obtained was cooled, broken up, and heated with a mixture of 8 parts of "880" ammonia, 79 parts of ethanol and 100 parts of water for 2 hours under reflux. After drying the solid in vacuum at 80°C for 16 hours, 14.1 parts of a white polymer were obtained. Upon heating 1.000 part of the sample in a bath at 222°C. and removing, cooling and weighing the sample at timed intervals it was found that this product lost 2% of its weight at a rate of 0.14% per minute and thereafter its first order degradation constant was 0.05% per minute.

The polymer was compression moulded at 170°C. for 3 minutes under 20 tons pressure to give a tough, bubble-free film 0.005 inch thick which could be flexed without cracking. The polymer could also be melt-spun at 170°C. to give strong fibres.

EXAMPLE X

Poly(decamethylene formal) was prepared by conventional formal interchange methods from 1,10-decamethylene glycol and dibutyl formal using p-toluene-sulphonic acid as catalyst.

A mixture of 1.3 parts of this formal with 12.9 parts of dry trioxane was prepared at 85°C. Into this mixture was injected a solution of 0.0084 part of boron trifluoride-diethyl etherate in 0.2 part of diethyl ether. After 4 hours, the solid was cooled, broken up and heated at reflux with 4 parts of

"880" ammonia, 40 parts of methanol and 50 parts of water for 3 hours.

The white powder obtained was filtered off, washed with acetone and dried at 65°C. in vacuum for 16 hours to give 7.7 parts of the polymer.

The polymer was heated to 222°C. as described in Example VIII. After a rapid initial loss in weight, the final first order breakdown rate of the polymer was 0.1% per minute.

Polymers having similar properties could be derived by the copolymerisation of trioxane with polyformals formed from polymethylene glycols containing from 6 to 12 methylene groups.

WHAT WE CLAIM IS:—

1. A copolymer comprising the product of polymerising a cyclic oligomer of formaldehyde with a polyformal as hereinbefore defined.

2. A copolymer according to claim 1 in which the cyclic oligomer of formaldehyde is trioxane.

3. A copolymer according to claim 1 or claim 2 in which the polyformal is derived from a diol containing an aromatic nucleus in the chain between two hydroxymethylene groups.

4. A copolymer according to claim 3 in which the polyformal is poly(p-xylylene glycol formal).

5. A copolymer according to claim 1 or claim 2 in which the polyformal is derived from a polymethylene glycol.

6. A copolymer according to claim 5 in which the polyformal is poly(ethylene glycol formal).

7. A copolymer according to claim 5 in which the polymethylene glycol contains from 6 to 12 methylene groups.

8. A copolymer according to claim 7 in which the polyformal is poly(decamethylene glycol formal).

9. A copolymer according to claim 1 or claim 2 in which the polyformal is derived from a diol containing ethylenic unsaturation in the chain between the hydroxyl groups.

10. A copolymer according to claim 9 in which the polyformal is poly(but-2-ene-1,4-diol formal).

11. A copolymer according to claim 1 in which the polyformal is derived from a cycloalkylene glycol.

12. A copolymer according to claim 11 in which the polyformal is poly(2,2,4,4-tetramethyl cyclobutane-1,4-diol formal).

13. A copolymer according to any of the preceding claims in which the polyformal has a molecular weight of at least 3,000.

14. A copolymer according to any of the preceding claims in which more than 80% molar but not more than 99.9% molar of

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- the units in the polymer chain are oxymethylene units.
15. A copolymer according to claim 14 in which from 90 to 99.5% molar of the units in the polymer chain are oxymethylene units.
16. A copolymer according to claim 15 in which from 95 to 98.5% molar of the units in the polymer chain are oxymethylene units.
17. A copolymer according to any of the preceding claims having an intrinsic viscosity of at least 1.0 as measured as a 0.5% solution in p-chlorophenol containing 2% of α -pinene at 60°C.
18. A copolymer according to any of the preceding claims in which the polymeric chains are substantially free from terminal oxymethylene hydroxide ($-\text{OCH}_2\text{OH}$) groups.
19. A copolymer according to claim 18 having a rate of loss in weight at 222°C. of less than 0.5% per minute, assuming First Order Kinetics.
20. A copolymer according to claim 19 having a rate of loss in weight at 222°C. after being initially heated at 222°C. for 20 minutes, of less than 0.1% per minute, assuming First Order Kinetics.
21. A copolymer comprising the product of copolymerising a cyclic oligomer of formaldehyde with a polyformal as hereinbefore defined, substantially as hereinbefore described and as illustrated in Examples I and II.
22. A copolymer comprising the product of polymerising a cyclic oligomer of formaldehyde with a polyformal as hereinbefore defined, substantially as hereinbefore described and as illustrated in Example III.
23. A copolymer comprising the product of polymerising a cyclic oligomer of formaldehyde with a polyformal as hereinbefore defined, substantially as hereinbefore described and as illustrated in Example VIII.
24. A copolymer comprising the product of polymerising a cyclic oligomer of formaldehyde with a polyformal as hereinbefore defined, substantially as hereinbefore described and as illustrated in Examples IV to VII and IX and X.
25. A copolymer according to any one of the preceding claims substantially as hereinbefore described with specific reference to any one aspect, feature or combination disclosed in the Specification and not specifically claimed in any one of claims 2 to 24.
26. A process for the manufacture of a copolymer containing oxymethylene units in which a cyclic oligomer of formaldehyde is copolymerised with a polyformal as hereinbefore defined in the presence of an electrophilic catalyst and no more than a very small amount of water.
27. A process according to claim 26 in which the cyclic oligomer of formaldehyde is trioxane.
28. A process according to claim 26 or claim 27 which is carried out in the presence of a solvent.
29. A process according to claim 28 in which the solvent is a hydrocarbon having at least 6 carbon atoms.
30. A process according to any of claims 26 to 29 in which the electrophilic catalyst is a Lewis acid.
31. A process according to claim 30 in which the electrophilic catalyst is boron trifluoride, alone or as a complex.
32. A process according to claim 31 in which the electrophilic catalyst is boron trifluoride-diethyl etherate.
33. A process according to any of claims 26 to 29 in which the electrophilic catalyst is ferric chloride.
34. A process according to any of claims 26 to 33 in which the catalyst is used in an amount of from 0.0001 to 0.1 part of active constituent per 100 parts of monomeric material.
35. A process according to any of claims 26 to 34 in which the polymerisation is effected at a temperature of from 50 to 90°C.
36. A process according to any of claims 26 to 35 in which the polymerisation is effected under conditions of shear.
37. A process according to any of claims 26 to 36 in which the polymerised mass is separated from the unreacted monomers and catalyst residues by solvent extraction.
38. A process according to any of claims 26 to 37 in which the copolymer is first freed from the catalyst residues and then heated in an inert atmosphere at a temperature of at least 160°C. to remove any terminal oxymethylene hydroxide ($-\text{OCH}_2\text{OH}$) groups.
39. A process according to claim 38 in which the copolymer is heated in the presence of a weak acid.
40. A process according to any of claims 26 to 37 in which the copolymer is treated with a solution of a base at elevated temperature to remove any terminal oxymethylene hydroxide ($-\text{OCH}_2\text{OH}$) groups.
41. A process according to claim 40 in which the base is ammonia.
42. A process according to claim 40 or claim 41 in which the copolymer before treatment is in a finely-divided state.
43. A process according to any of claims 40 to 42 in which the copolymer is dissolved in the solution of the base.
44. A process according to claim 43 in which the solvent is a mixture of water with a water-miscible alcohol, a water-miscible ketone or an ether.
45. A process according to claim 44 in which the solvent is a mixture of water and methanol.
46. A process according to any of claims

- 40 to 45 in which the treatment is effected under reflux.
47. A process according to any of claims 26 to 37 in which the copolymer is then end-group stabilised.
48. A process according to claim 47 in which the copolymer is reacted with a carboxylic acid anhydride.
49. A process according to any of claims 26 to 48 in which the polyformal is derived from a polymethylene glycol.
50. A process according to claim 49 in which the polyformal is derived from ethylene glycol.
51. A process according to claim 49 in which the polymethylene glycol contains from 6 to 12 methylene groups.
52. A process according to claim 51 in which the polyformal is derived from 1,10-decamethylene glycol.
53. A process according to any of claims 26 to 48 in which the polyformal is derived from a diol having an aromatic nucleus between two hydroxymethylene groups.
54. A process according to claim 53 in which the polyformal is derived from p-xylylene glycol.
55. A process according to any of claims 26 to 48 in which the polyformal is derived from a diol containing ethylenic unsaturation in the chain between the hydroxyl groups.
56. A process according to claim 55 in which the polyformal is derived from but-2-ene-1,4-diol.
57. A process according to any of claims 26 to 48 in which the polyformal is derived from a cyclo-alkylene glycol.
58. A process according to claim 57 in which the polyformal is derived from 2,2,4,4-tetramethyl cyclobutane-1,3-diol.
59. A process for the manufacture of a copolymer in which a cyclic oligomer of formaldehyde is subjected to polymerising conditions together with a polyformal as hereinbefore defined and in the presence of an electrophilic catalyst and no more than a very small amount of water, substantially as hereinbefore described and as illustrated in Examples I and II.
60. A process for the manufacture of a copolymer in which a cyclic oligomer of formaldehyde is subjected to polymerising conditions together with a polyformal as hereinbefore defined and in the presence of an electrophilic catalyst and no more than a very small amount of water, substantially as hereinbefore described and as illustrated in Example III.
61. A process for the manufacture of a copolymer in which a cyclic oligomer of formaldehyde is subjected to polymerising conditions together with a polyformal as hereinbefore defined and in the presence of an electrophilic catalyst and no more than a very small amount of water, substantially as hereinbefore described and as illustrated in Example VIII.
62. A process for the manufacture of a copolymer in which a cyclic oligomer of formaldehyde is subjected to polymerising conditions together with a polyformal as hereinbefore defined and in the presence of an electrophilic catalyst and no more than a very small amount of water, substantially as hereinbefore described and as illustrated in Examples IV to VII and IX and X.
63. A process according to any of claims 26 to 62, substantially as hereinbefore described with specific reference to any one aspect, feature or combination disclosed in the specification and not specifically claimed in any of claims 27 to 62.
64. A moulded article derived from a solid copolymer comprising the product of polymerising a cyclic oligomer of formaldehyde with a polyformal as hereinbefore defined.
65. An extruded article derived from a solid copolymer comprising the product of polymerising a cyclic oligomer of formaldehyde with a polyformal as hereinbefore defined.
66. A film derived from a solid copolymer comprising the product of polymerising a cyclic oligomer of formaldehyde with a polyformal as hereinbefore defined.
67. A fibre derived from a solid copolymer comprising the product of polymerising a cyclic oligomer of formaldehyde with a polyformal as hereinbefore defined.
- BERTRAM F. DREW,
Agent for the Applicants.